NMR[14] (C_6D_6) 66.48 (d, OCH_2, $^{2}J_{PC}$ = 7.33 Hz), 50,34 (d, NCH_2CH_2Cl, $^{2}J_{PC}$ = 2.44 Hz), 49.31 (d, $N(CH_2CH_2Cl)_2$, $^{2}J_{PC}$ = 4.89 Hz), 47.57 (s, NCH_2CH_2Cl), 42.32 (s, $N(CH_2CH_2Cl)_2$), 41.48 (d, $NCH_2CH_2CH_2O$, $^{2}J_{PC}$ = 3.66 Hz), 26.04 ppm (d, $NCH_2CH_2CH_2O$, $^{3}J_{PC}$ = 3.66 Hz) and (+)-**3** from diastereomer B (64.4% yield; $[\alpha]^{25}{}_{589}$ +30.1° (*c* 3.535, MeOH)). The ^{31}P NMR (C_6D_6) and ^{13}C NMR (C_6D_6) spectra of (+)-**3** are identical with those of (−)-**3** and both enantiomers are colorless oils. The chemical purity of the enantiomers is demonstrated by the NMR data and a single TLC spot using a 2:1 ratio of CH_2Cl_2-Me_2CO as a development solvent (R_f 0.53). The enantiomers are optically pure according to FT ^{31}P NMR spectroscopy. Thus a 1:1 molar ratio of (±)-**3** to EuOpt-I (Willow Brook Laboratories) shift reagent as a 0.2 M solution in C_6D_6 exhibited two well-defined peaks at −107.21 and −108.73 ppm. Under the same conditions, the enantiomers gave only the −108.73-ppm peak for (+)-**3** and the −107.21-ppm peak for (−)-**3**.

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(13) ^{31}P chemical shifts are relative to 85% H_3PO_4 as external standard.
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Electrochemistry in Ordered Systems. 1. Oxidative Electrochemistry of 10-Methylphenothiazine in Anionic, Cationic, and Nonionic Micellar Systems

Sir:

Electron-transfer reactions of phenothiazine derivatives of interest in physiological[1] and photoionization studies[2] have been examined in both aqueous[3] and nonaqueous[4] media. We report herein the effects on the redox properties of 10-methylphenothiazine (MPTH) resulting from solubilization of this substrate in anionic, cationic, and nonionic surfactants.[5] Relative to voltammetric behavior in aqueous media,[6] the addition of either cationic or nonionic surfactants causes no significant shift in the differential pulse voltammetric (DPV) peak potentials for the one-electron oxidation of MPTH to the corresponding cation radical ($MPTH^{+}\cdot$).[7] This invariance of peak potential indicates the absence of preferential interactions[9] between either MPTH or $MPTH^{+}\cdot$ and surfactant in both cationic and nonionic micellar systems.[10]

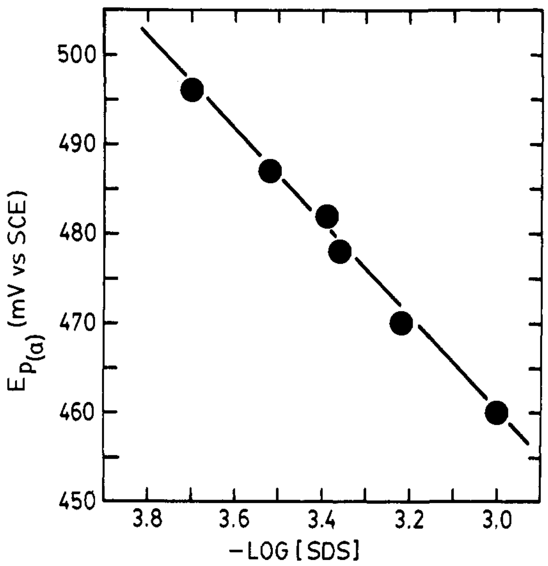

Figure 1. Dependence of DPV peak potential for the oxidation of 20 μM MPTH on SDS concentration in 0.05 M $LiClO_4$: slope = −53 (±3) mV; intercept = 303 (±7) mV; coefficient of correlation = 0.9962.

In anionic SDS systems, however, the DPV peak potential for the oxidation of MPTH to $MPTH^{+}\cdot$ was found to vary linearly with the logarithm of the SDS concentration up to the cmc (Figure 1) and to remain invariant at surfactant concentrations in excess of this value. Alterations of the peak potential can be expected as a result of preferential interaction between the medium and one member of the redox couple.[9] For an oxidation process, a cathodic shift reflects increased ease of oxidation and is attributable to stabilization of the oxidized member of the couple (i.e., $MPTH^{+}\cdot$). Below the cmc, the extent of surfactant aggregation is minimal and such solutions may be viewed as being comprised of free monomeric surfactant species.[8] Hence the variation of peak potential with surfactant concentration *below* the cmc points to an interaction between monomeric dodecyl sulfate anion (DS^{-}) and $MPTH^{+}\cdot$. Above the cmc, monomer concentration remains essentially unchanged with newly added surfactant resulting in increased numbers of micelles.[8a] That the DPV peak potential above the cmc is unaltered by added surfactant reflects invariance of the microenvironment experienced by the solubilized MPTH and resulting $MPTH^{+}\cdot$

To assess the relative stability of $MPTH^{+}\cdot$ in the surfactant systems addressed in this work, the rates of decay of $MPTH^{+}\cdot$ in H_2O, H_2O-$LiClO_4$, H_2O-KBr, SDS-$LiClO_4$, Brij-$LiClO_4$, and CTAB-KBr were measured. The half-lives for the solvolyses of $MPTH^{+}\cdot$ in these media (Table I) show that of the cation radical in the anionic surfactant system to be ca. twice that observed in comparable aqueous medium. Grätzel et al.[2c] reported $MPTH^{+}\cdot$ to be extremely stable in SDS micelles, decaying <20% in 24 h. The more rapid decay of $MPTH^{+}\cdot$ in SDS described here may be a manifestation of supporting electrolyte ($LiClO_4$) on micelle structure.[8a] Indeed, in the

Table I. Half-Life of $MPTH^{+}\cdot$ in Media of Interest to This Work[a]

medium	$t_{1/2}$, h[b]
H_2O	8.8 (±0.3)[c]
$LiClO_4$ (0.05 M)	9.9 (±0.6)
KBr (0.05 M)	7.2 (±0.8)
CTAB (4.9 mM)-KBr (0.05 M)	1.4 (±0.2)
Brij-35 (2020 mg %)-$LiClO_4$ (0.05 M)	2.5 (±0.5)
SDS (20 mM)-$LiClO_4$ (0.05 M)	17.2 (±0.6)

[a] $[MPTH^{+}\cdot]_0 \simeq 5 \times 10^{-5}$ M, introduced as perchlorate salt.[11] Decay kinetics monitored spectrophotometrically at 516 nm. [b] Mean of triplicate determinations at 25 °C. [c] Average deviation.

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presence of 0.05 M $LiClO_4$ the cmc of SDS is approximately fivefold less than that determined in water alone.[12] The enhanced rates of decay of $MPTH^{+}\cdot$ in the cationic and nonionic surfactant systems relative to those seen in the base electrolytes in the absence of surfactant are suggestive of micellar catalysis in these systems.[13]

The observed dependence of the DPV peak potential for the oxidation of MPTH at pre-cmc concentration levels of SDS lends itself to quantitation of both the stoichiometry and the formation constant of the cation radical-surfactant complex. For the oxidation of MPTH in the presence of SDS, the system may be represented as

$$\mathrm{MPTH} \rightleftharpoons \mathrm{MPTH}^{+}\cdot + e^{-} \qquad (1)$$

$$\mathrm{MPTH}^{+}\cdot + p\mathrm{DS}^{-} \overset{K}{\rightleftharpoons} (\mathrm{MPTH}^{+}\cdot)(\mathrm{DS}^{-})_{p} \qquad (2)$$

At 25 °C, the dependence of the peak potential for the oxidation of MPTH on the concentration of SDS is given by[9,14]

$$E_{\mathrm{p(a)}}' = E_{\mathrm{p(a)}}^{\circ} - 0.059 \log K - 0.059(p) \log [\mathrm{SDS}] \qquad (3)$$

where $E_{\mathrm{p(a)}}'$ is the DPV peak potential in the presence of SDS and $E_{\mathrm{p(a)}}^{\circ}$ is that observed in its absence. The data shown in Figure 1 affords a least-squares slope of −53 (±3) mV which corresponds to $p \simeq 1$ indicating a stiochiometry of one dodecyl sulfate anion per 10-methylphenothiazine cation radical.[14c] From the least-squares intercept of these data (303 (±7) mV) and the value of $E_{\mathrm{p(a)}}^{\circ}$ observed in 0.05 M $LiClO_4$,[7] the formation constant for the $(MPTH^{+}\cdot)(DS^{-})$ complex evaluates as 2.0×10^{3} M^{-1}. It is important to note that this formation constant reflects interaction between $MPTH^{+}\cdot$ and monomeric dodecyl sulfate entities, not between $MPTH^{+}\cdot$ and micelles.[15]

This interaction between $MPTH^{+}\cdot$ and dodecyl sulfate anion suggests the site of solubilization of $MPTH^{+}\cdot$ in SDS micelles to be the Stern region wherein the charged head groups of the surfactant reside. Examination of the ultraviolet absorption maxima of $MPTH^{+}\cdot$ in aqueous, micellar SDS, and hydrocarbon media provides insight concerning the site of solubilization of the cation radical. These data[16] suggest that, in micellar SDS systems, $MPTH^{+}\cdot$ resides in a highly polar environment rather than in the hydrocarbon "core" of the micelle.[17] While models for micelle structure remain in question,[18] the results reported here are consistent with an "open" structure which allows both $MPTH^{+}\cdot$ and water to be interspersed among the aggregated surfactant molecules.[18,19]

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(6) "Aqueous media" refers to SDS or Brij-35 in 0.05 M $LiClO_4$ and CTAB in 0.05 M KBr. CTAB is not soluble in $LiClO_4$ solution.

(7) At a platinum electrode at 25.0 °C. DPV peak potential (vs. SCE) for the MPTH/$MPTH^{+}\cdot$ couple in 0.05 M $LiClO_4$ is 0.498 (±0.004) and in 0.05 M KBr is 0.522 (±0.003) V. DPV peak potentials for this couple in Brij–$LiClO_4$ and CTAB–KBr *were* 0.512 (±0.023) and 0.535 (±0.011) V, *respectively*, at surfactant concentrations spanning the critical micelle concentrations (cmc's).[8]

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(15) Evans, C. A.; Bolton, J. R. (*J. Am. Chem. Soc.* **1977,** *99*, 4502–4504) have shown strong interaction between *N*-methylphenazonium cation radical and SDS *micelles* ($K \simeq 10^{5}$ M^{-1}).

(16) In H_2O, $\lambda_{\max}^{MPTH^{+}\cdot}$ 269 (±1); in 0.05 M $LiClO_4$, 270 (±1); in 20 mM SDS–0.05 M $LiClO_4$, 271 (±1); in *n*-heptane, 254 (±1); in *n*-pentane, 256 (±1) nm.

(17) Evans and Bolton[15] report the mean residence position of *N*-methylphenazonium cation radical to be "in the hydrocarbon region a few ångstroms below the head groups".

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Photoelectrochemical Reduction of *N,N'*-Dimethyl-4,4'-bipyridinium in Aqueous Media at p-Type Silicon: Sustained Photogeneration of a Species Capable of Evolving Hydrogen

Sir:

We report here a new approach to the energetically uphill generation of H_2 from H_2O. There have been numerous recent claims concerning chemical systems for the photoinduced evolution of H_2 from aqueous media, but in many of the systems reported there are sacrificial reducing agents used which cloud the overall thermodynamics and preclude sustained evolution of H_2.[1-6] However, these studies have resulted in several interesting procedures for manipulating charge-transfer kinetics such that generation of H_2 is possible by schemes such as that represented:[6]

$$\mathrm{PQ}^{2+} \xrightarrow[\text{[sacrificial reagent(s)]}]{\text{light}} \mathrm{PQ}^{+}\cdot \qquad (1)$$

$$2\mathrm{H_2O} + 2\mathrm{PQ}^{+}\cdot \xrightarrow[\substack{\text{[catalyst]} \\ \text{pH<7}}]{\Delta} 2\mathrm{PQ}^{2+} + \mathrm{H_2}\uparrow + 2\mathrm{OH}^{-} \qquad (2)$$

$$\mathrm{PQ}^{2+} \equiv N,N'\text{-dimethyl-4,4'-bipyridinium}$$

We are prompted by these studies to report the sustained photogeneration (without sacrificial reagents) of $PQ^{+}\cdot$ in aqueous solutions using a p-type Si photocathode in an electrochemical cell. p-type semiconductors are known to be capable of serving as photocathodes for direct H_2 production,[7] but a survey of the literature reveals that p-type materials

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